Preparation and X-ray Structure of a Mixed-Metal Double-Cubane-Type Aqua Ion, $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$

Takashi Shibahara,* Haruo Akashi, and Hisao Kuroya

Department of Chemistry, Okayama University of Science
1-1 Ridai-cho, Okayama 700, Japan

Received December 1, 1987

It is well known that both the molybdenum and copper are essential elements in biological systems, functioning antagonistically. In the meantime a number of complexes characteristically containing molybdenum, copper, and sulfur have been prepared.[1] We have reported the reaction of $Mo_3S_4(aq)^{4+}$ aqua ion (**1**)[2] with iron,[3] nickel,[4] and magnesium,[5] the product being $Mo_3FeS_4(aq)^{4+}$, $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, and $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$, respectively. In this paper, we describe the preparation and properties of a mixed-metal double-cubane-type cluster compound, $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$ (**2**), prepared by the reaction of the aqua ion **1** with metallic copper. An X-ray structure of $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9](CH_3\cdot C_6H_4\cdot SO_3)_8\cdot 20H_2O$ (**2′**) has been determined. A structure determination of $[Mo_3CuS_4((S_2P(OC_2H_5)_2)_3)(I)(CH_3COO)(HCON(CH_3)_2)]$ containing the Mo_3CuS_4 core[6] has been reported previously. Reference should be made also to another cubane-type Mo-Cu-S cluster of $[(Cu_3MoS_3Cl)(PPh_3)_3S]$.[7]

For the preparation of **2**, all the experiments were carried out under a dinitrogen atmosphere. Procedures similar to those in the preparation of $Mo_3FeS_4(aq)^{4+}$ [3] were applied until, after the stage of Dowex 50W-X2 separation,[8] a red-brown solution was obtained by use of 1 M HCl. Then, the solution was absorbed on the cation exchanger again and eluted with 4 M HPTS (*p*-toluenesulfonic acid). The resultant solution was kept in a refrigerator, and dark brown crystals of **2′** were obtained in a few days.[9]

X-ray structure analysis[10] of **2′** revealed the existence of a double-cubane-type core of $(Mo_3CuS_4)_2$ in which the copper atoms are bridged by two sulfur atoms with a short Cu-Cu distance (2.426 (5) Å) as shown in Figure 1. A center of symmetry resides on the midpoint of the two copper atoms. The Cu-Cu distance is shorter than that in metallic copper (2.56 Å). The Cu has a distorted tetrahedral geometry, if possible Mo-Cu and Cu-Cu bonds are ignored. The coordination number of the bridging sulfur, S1, is four, while that of the other sulfurs are three.[11]

The compound **2′** is paramagnetic (μ_{eff} = 2.76 μ_B per double cubane) and obeys the Curie-Weiss law down to the liquid nitrogen temperature. The XPS measurement on Cu-$2p_{3/2}$ bonding energy (934.2 eV) indicates that the oxidation state of Cu is plus one.[12] On the basis of this, a formal oxidation state of Mo_3(IV,IV,III) or a mean oxidation state of Mo(+3.67) is ascribed to each of the cubane-type Mo_3CuS_4 moieties. It seems that the paramagnetism comes formally from the molybdenum atoms.

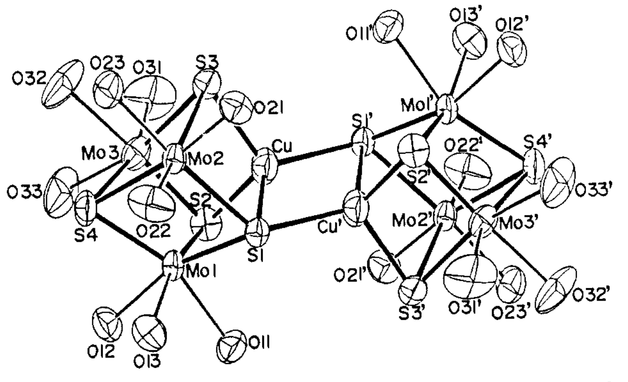


Figure 1. Perspective view of $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$ cation with selected interatomic distances (Å) and angles (deg): Mo1-Mo2, 2.738 (2); Mo1-Mo3, 2.722 (2); Mo2-Mo3, 2.730 (2); Mo1-Cu, 2.952 (2); Mo2-Cu, 2.930 (2); Mo3-Cu, 2.778 (2); Mo1-S1, 2.354 (3); Mo1-S2, 2.342 (4); Mo1-S4, 2.320 (3); Mo2-S1, 2.361 (3); Mo2-S3, 2.338 (4); Mo2-S4, 2.327 (4); Mo3-S2, 2.333 (4); Mo3-S3, 2.351 (4); Mo3-S4, 2.339 (4); Cu-S1, 2.457 (4); Cu-S2, 2.226 (4); Cu-S3, 2.222 (3); Cu-Cu′, 2.426 (5); Cu-S1′, 2.296 (6); Mo-O(H_2O), 2.17 [2]; S1-Cu-S2, 99.1 (2); S1-Cu-S3, 100.2 (2); S2-Cu-S3, 107.7 (2); S1′-Cu-S1, 118.7 (2); S1′-Cu-S2, 113.8 (2); S1′-Cu-S3, 115.3 (2); Cu-S1-Cu′, 61.3 (1). (The primed atoms are related to the unprimed ones by a center of symmetry.)

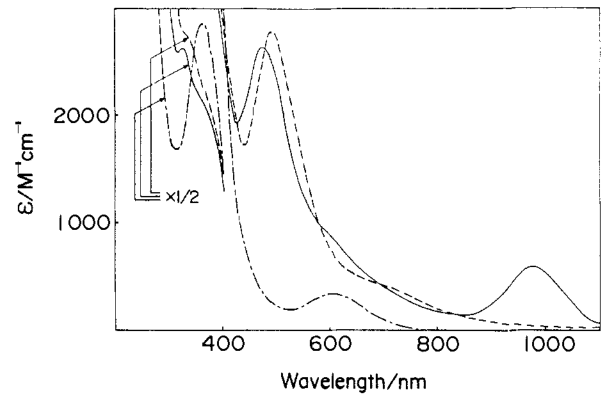


Figure 2. Electronic spectra: (—) **2′** dissolved in 2 M HPTS; (- -) **2′** dissolved in 1 M HCl; (— - —) $Mo_3S_4(aq)^{4+}$ in 2 M HPTS.

Figure 2 shows the electronic spectrum of **2′** in 2 M HPTS [$\lambda_{max,nm}$ (ϵ/M^{-1} cm^{-1} per double cubane) 325 (5254), 360 (sh, 4376), 470 (2652), 620 (sh, 740), and 975 (589)] and that in 1 M HCl [330 (sh, 5520), 370 (sh, 4350), 490 (2797), 710 (sh, 401)] together with that of **1** in 2 M HPTS. The peak of **2** in 2 M HPTS at 975 nm disappears when either the medium is replaced by 1 M HCl or a few drops of concentrated HCl is added to the HPTS solution,[13] though the remaining parts of the spectra of **2′** in both media are similar to each other. The compound **2′** dissolves sparingly in HPTS solution but easily in HCl solution. The formation mechanism of **2** therefore can be as follows: the reaction of **1** with metallic copper in HCl medium gives a "single" cubane-type mixed-metal ion in which the chloride ion is coordinated to the copper atom, and then, when the medium is changed from HCl to HPTS, two "single" cubane-type ions are combined to afford **2** by the formation of sulfur bridges through the loss of chloride ion out of the copper atom. Conversely, the Cu-S1′ (and Cu′-S1) bond (Figure 1) is cleaved readily by the coordination of the Cl^- ion to Cu of the $(Mo_3CuS_4)_2$ core in 1 M HCl solution.[14] It is interesting that the aqua ion **1** in HCl acts catalytically for

---

(1) For example: Clarke, N. J.; Laurie, S. H.; Pratt, D. E. *Inorg. Chim. Acta* **1987**, *138*, 103-104. An excellent review has appeared: Sarkar, S.; Mishra, S. B. S. *Coord. Chem. Rev.* **1984**, *59*, 239-264.

(2) For convenience, the term "aqua ion" will be used here for species in which bridging sulfur atoms exist and other ligands are only water.

(3) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342-1343.

(4) Shibahara, T.; Kuroya, H. *Abstracts of Papers*, 1987 International Miniconference for Young Chemists in Tokyo—Macrocyclic and Coordination Chemistry, Tokyo, July 1987.

(5) Shibahara, T.; Yamamoto, T.; Kanadani, H.; Kuroya, H. *J. Am. Chem. Soc.* **1987**, *109*, 3495-3496.

(6) Xintao, W.; Shaofeng, L.; Lianyong, Z.; Qjangjin, W.; Jiaxi, L. *Inorg. Chim. Acta* **1987**, *133*, 39-42.

(7) Muller, A.; Bogge, H.; Schimanski, U. *J. Chem. Soc., Chem. Commun.* **1980**, 91-92.

(8) The solution of **1** containing metallic Cu was left for 3-7 days before separation, the color having turned from green to red-brown.

(9) Anal.: C, 22.30; H, 3.87. Calcd for **2′**: C, 22.32; H, 4.41.

(10) Crystal data: triclinic system, space group $P\bar{1}$, a = 15.628 (7) Å, b = 16.792 (7) Å, c = 11.978 (4) Å, α = 96.03 (3)°, β = 108.52 (3)°, γ = 101.42 (4)°, V = 2874 (2) Å^3, Z = 1. The structure was solved by direct method (MULTAN) and refined by least squares to a current R value of 0.0683 for 5310 reflections ($F_o \geq 8\sigma(F_o)$). Details will be reported elsewhere.

(11) Vahrenkamp, H. In *Sulfur, Its Significance for Chemistry, for Geo-, Bio-, and Cosmosphere and Technology*; Muller, A., Krebs, B., Eds.; Amsterdam, 1984; pp 121-139.

(12) Cf. ref 1; standard: C-1s (285.0 eV).

(13) The reaction of **2** with Cl^- is very rapid, and the color of the HPTS solution (dark-brown) changes to red-brown instantaneously on the addition of hydrochloric acid.

(14) **2** is eluted slower than **1** (charge: 4+) by 2 M HPTS solution and earlier than **1** by 1 M HCl solution from the cation exchange resin.

0002-7863/88/1510-3313$01.50/0

the air-oxidation of Cu metal to Cu^{2+} ion.

Short Cu–Cu distances have been found in many di- or polynuclear Cu(I) complexes. However, all of these complexes have bridging ligands between copper atoms.[15,16] Moreover, MO calculations have not acknowledged the existence of direct Cu(I)–Cu(I) bonding of any significance.[15-17] The peak at 975 nm, therefore, may be due to charge-transfer between S1′ and Cu and not to the excitation of the electron in the Cu–Cu bonding orbital. More detailed studies are required to explain the nature of this peak.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (no. 62470043) from the Ministry of Education, Science and Culture.

Supplementary Material Available: X-ray crystallographic data, results of cyclic voltammetry and magnetic measurements, and listings of bond angles and bond lengths for **2′** (8 pages). Ordering information is given on any current masthead page.

---

(15) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 800.

(16) Clusters with Cu_8S_{12} core in which the copper atoms are bridged by sulfur atoms have also been reported: Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* **1977**, *99*, 6268–6280.

(17) For example: Mehrotra, P.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187–2189.

A New Class of Homoleptic 12-Electron Molybdenum and Tungsten Alkoxide Clusters of Formula $[M_4(OR)_{12}]$

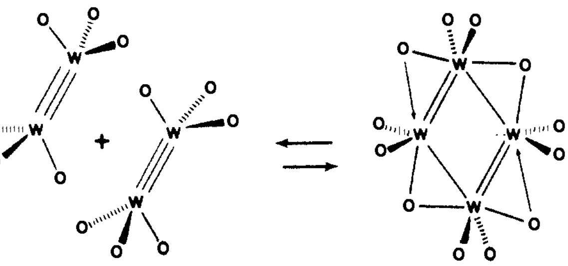
M. H. Chisholm,* K. Folting, C. E. Hammond, and M. J. Hampden-Smith

Department of Chemistry and Molecular Structure Center Indiana University, Bloomington, Indiana 47405

Received February 8, 1988

We are interested in developing efficient synthetic routes to alkoxide-supported molybdenum and tungsten clusters that may prove to be excellent models for fragments of reduced oxides of the same metals.[1] These clusters should include both coordinative unsaturation and redox flexibility at the metal centers to initiate organometallic chemistry upon substrate reduction. Complementary metal oxide model systems such as polyoxoanions may prove effective for oxidation catalysis.[2]

We have recently demonstrated that $W_2(O\text{-}i\text{-}Pr)_6$ (I) exists in reversible equilibrium with its 12-electron cluster $W_4(O\text{-}i\text{-}Pr)_{12}$ (II) in solution at room temperature, eq 1,[3] whereas $Mo_2(O\text{-}i\text{-}Pr)_6$ is indefinitely stable with respect to cluster formation.[4]



(1)

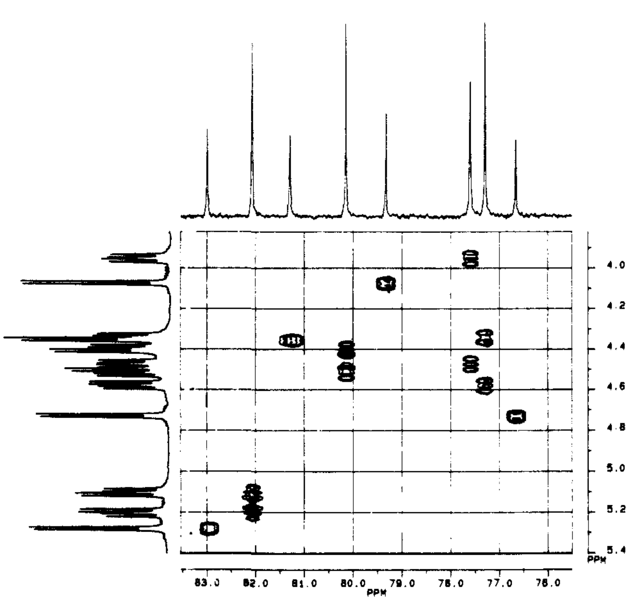


Figure 1. The ^{13}C–^{1}H 2D heteronuclear chemical shift correlated contour plot of the methylene region of XI showing the eight types of alkoxide ligands in the ratio 1:1:1:1:2:2:2:2. The carbon resonances of relative intensity 2 have inequivalent methylene protons. Spectrometer frequency = 500.13 MHz (^{1}H); 2D matrix: [1K (84 scans) × 256].

Even by reducing the steric demands at the molybdenum center we were unable to induce the formation of new metal–metal bonds in $[Mo_2(O\text{-}i\text{-}Pr)_5(OMe)]_2$ (III), which instead retains isolated, unbridged Mo–Mo triple bonds.[5] We report here the isolation and characterization of members of a new class of 12-electron tetranuclear alkoxide clusters, IV–XI, which are spectroscopically isostructural for both molybdenum *and* tungsten together with the single-crystal X-ray diffraction structure of one derivative, $[Mo_4(O\text{-}CH_2\text{-}c\text{-}Bu)_{12}(HO\text{-}CH_2\text{-}c\text{-}Bu)]$ (XI) (where c-Bu = cyclobutyl). This represents the first group of structurally related homoleptic alkoxide clusters for molybdenum and tungsten in oxidation state (3+).

Treatment of hexane solutions of $M_2(O\text{-}t\text{-}Bu)_6$ where M = Mo or W with >6 equiv of any of the alcohols, $HOCH_2R$, where R = cyclohexyl (Cy), isopropyl (*i*-Pr), cyclopentyl (Cp), or cyclobutyl (c-Bu), at room temperature results in immediate darkening of the solution to a deep green color. After having been stirred for 4 h, the volatile components are removed in vacuo, and by dissolving the residue in the minimum amount of 1,2-dimethoxyethane the following products crystallized upon cooling (−20 °C): $W_4(OCH_2\text{-}Cy)_{12}$ (IV), $W_4(OCH_2\text{-}i\text{-}Pr)_{12}$ (V), $W_4(OCH_2\text{-}Cp)_{12}$ (VI), $W_4(OCH_2\text{-}c\text{-}Bu)_{12}$ (VII), $Mo_4(OCH_2\text{-}Cy)_{12}$ (VIII), $Mo_4(OCH_2\text{-}i\text{-}Pr)_{12}$ (IX), $Mo_4(OCH_2\text{-}Cp)_{12}$ (X), and $Mo_4(OCH_2\text{-}Bu)_{12}$ (XI), respectively.[6]

The ^{1}H and ^{13}C NMR spectra of all these complexes, IV–XI, are consistent with a common, stereochemically *rigid* structural $[M_4O_{12}]_n$ unit in solution. In the ^{1}H NMR spectrum there is evidence for eight types of alkoxide ligands from the methylene proton resonances which are in the relative ratios 1:1:1:1:2:2:2:2. The resonances of relative intensity 2 arise from diastereotopic methylene protons, while those of intensity 1 are nondiastereotopic and can be distinguished at a spectrometer frequency of 500 MHz. A ^{13}C–^{1}H 2D heteronuclear chemical shift correlated contour plot (see Figure 1) clearly demonstrates the eight different types of alkoxide ligands as well as the relationship between the proton and carbon resonances. Thus the molecule contains a mirror plane of symmetry and is of lower symmetry than was observed for $W_4(O\text{-}i\text{-}Pr)_{12}$ (II). The elemental analyses are consistent with the empirical formula $[W(OR)_3]_n$, and the spectroscopic data dictate that the value of n is a multiple of four, e.g., $W_4(OR)_{12}$, $W_8(OR)_{24}$, ..., etc.[7] To establish the detailed nature of this new

---

(1) Chisholm, M. H.; Folting, K.; Eichhorn, B. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 3146 and references therein.

(2) Pope, M. T. In *Heteropoly and Isopoly Oxometallates*; Springer: New York, 1983. Day, V. W.; Klemperer, W. G.; Schwartz, C.; Wang, R. C. NATO Workshop Report, in press. Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.

(3) Chisholm, M. H.; Clark, D. L.; Folting, K.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1014. Chisholm, M. H.; Clark, D. L.; Folting, K.; Hampden-Smith, M. J.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 775; Chisholm, M. H.; et al. *J. Am. Chem. Soc.* submitted for publication.

(4) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

(5) Chisholm, M. H.; Hammond, C. E.; Hampden-Smith, M. J.; Huffman, J. C.; Van Der Sluys, W. G. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 904.

(6) Satisfactory elemental analyses have been obtained.